

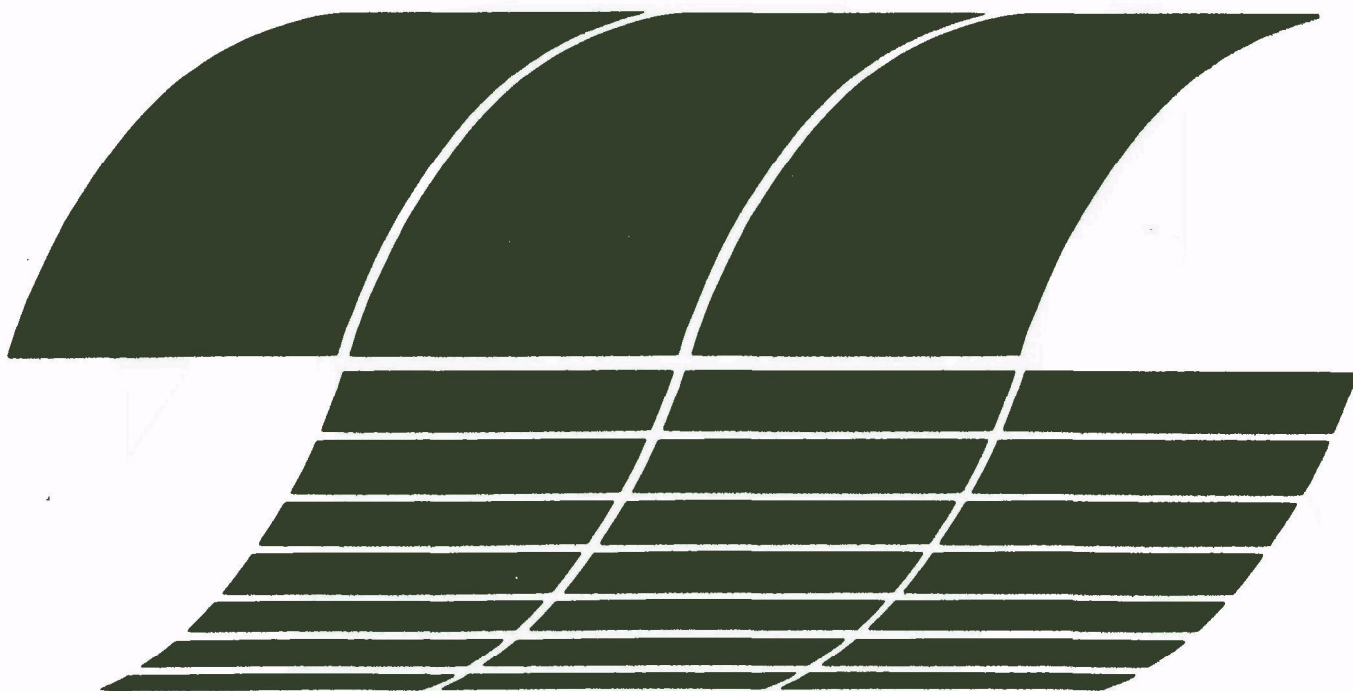
Research and Development



# Quality Assurance in Support of Energy Related Monitoring Activities in the Western United States

## Annual Report No. 1

### Interagency Energy/Environment R&D Program Report



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QUALITY ASSURANCE IN SUPPORT OF ENERGY  
RELATED MONITORING ACTIVITIES IN THE  
WESTERN UNITED STATES

Annual Report No. 1

by

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## ABSTRACT

The purpose of the program is to establish a quality assurance data base for ambient air monitoring in specified geographical areas around present and proposed energy development projects, and to provide technical assistance to enable existing monitoring networks to achieve a high level of data quality. A goal of the program is to enable the government to utilize and compare air monitoring data from diverse sources for future study and planning purposes by providing information concerning data quality from the individual monitoring networks.

An initial on-site review of 18 laboratories and associated field sites was completed, and detailed evaluation reports containing a list of recommendations for eliminating observed deficiencies were submitted to EPA.

Regularly scheduled laboratory performance surveys are being carried out for the analysis of sulfate, nitrate,  $\text{SO}_2$ ,  $\text{NO}_2$ , and CO and for weight measurement and high volume flow rate. In these surveys audit samples or devices are submitted to participating laboratories and their results are compared with those obtained by Rockwell.

Approximately 10% of the analyses performed by another laboratory for metals collected in high volume filters are being repeated by Rockwell. The causes for observed large differences in the analysis of synthetic metal samples prepared by Rockwell are being investigated.

Quarterly field audits are being conducted at specified monitoring sites. Known concentrations of pollutants are delivered to each continuous analyzer, and the observed response is compared with that predicted by the agency's calibration. Procedures have been developed to assure reliable performance by the audit devices and standards. Additional checks on the equipment and procedures are made by means of quarterly audits performed in the EPA/EMSL laboratory at Research Triangle Park, North Carolina.

Approximately 70 site audits have been completed, and audit reports have been submitted to EPA. Satisfactory results were found most frequently in audits of CO, CH<sub>4</sub>, and total hydrocarbon analyzers. The most unsatisfactory results were found in audits of NO<sub>2</sub>, NO<sub>x</sub>, NO, and SO<sub>2</sub> analyzers.

Technical assistance has been provided to participating agencies, as requested by the Project Officer. The assistance consists mainly of instruction manuals, procedures, or literature references relating to chemical analysis or quality assurance. Much of the technical assistance was given informally during site visits. Assistance was also provided concerning specific laboratory and calibration problems during visits to Rockwell AMC by personnel from participating agencies. A brief description of these and other types of technical assistance is given in the report.

This report was submitted in fulfillment of Contract No. 68-02-2412 by Rockwell International Air Monitoring Center under the sponsorship of the U. S. Environmental Protection Agency. This report covers the period July 13, 1976 to September 30, 1977. Work under this contract will continue to July 13, 1981.

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# SECTION 1

## INTRODUCTION

This report describes and summarizes the activities and achievements of Rockwell International Air Monitoring Center during the first year of the Contract No. 68-02-2412 titled Quality Assurance in Support of Energy Related Monitoring Activities in the Western United States. The effective date of the contract was July 13, 1976, and the program is scheduled to be completed on July 13, 1981.

On June 16, 1977, the contract was expanded to include additional evaluations and field audits sites located in Colorado, Utah, and Montana. On August 9, 1977, the contract was further expanded to include on-site inspection and evaluation of seven water quality field stations of the U. S. Geological Survey in the states of Arizona, Colorado, Montana, New Mexico, North Dakota, Utah, and Wyoming.

The activities described in this report cover generally the period from the beginning of the program to approximately the end of September 1977. For convenience the title of the program is shortened to Western Quality Assurance Program.

The purpose of the Western Quality Assurance Program is to develop and implement a quality assurance program for use by networks monitoring air quality around present and proposed energy development projects. These energy projects are located in the states of Montana, South Dakota, North Dakota, Wyoming, Utah, Colorado, Arizona, Nevada, New Mexico, and California.

A goal of the program is to enable the government to utilize and compare air monitoring data from diverse sources for future study and planning purposes by providing information concerning data quality from the individual monitoring networks.



This Annual Report is written as a general overview of performance and progress thus far. As such it is not intended to treat all areas in specifics nor will it treat each area rigorously. In order to keep this report within manageable size, the reader will oftentimes be directed to specific reports, available in EPA files, should greater detail be required.

The Western Quality Assurance Program is divided into four task areas involving:

- 1) An initial on-site review of laboratories and field sites
- 2) A sample submissions audit program to the laboratories
- 3) On-site field calibration audits; and
4. Technical assistance to the laboratories, as required.

All the work carried out by Rockwell in connection with these tasks is summarized in the following sections. Section 2.0 describes the on-site evaluations; Section 3.0 discusses the results of the interlaboratory performance surveys; Section 4.0 summarizes field audit results, Section 5.0 describes technical assistance given to the various agencies; and Section 6.0 outlines the plans for next year.

## SECTION 2

### SITE EVALUATIONS

Pursuant to provisions of the Western Quality Assurance Program Contract, laboratories and field sites were visited, inspected and evaluated by Rockwell personnel. Visits were made to the 18 agencies listed in Table 1. Three of the agencies - - Montana, Utah, and Colorado - - were visited a second time as a result of the expansion in June 1977 in the number of sites audited.

A detailed report covering the site evaluations has been made for each agency, and each agency has been given the opportunity to comment upon the preliminary draft of the report. When appropriate, these comments were noted and used in preparing the final report, copies of which were sent to the EPA. The final report contains a great deal of information concerning organization, staffing, laboratory and field equipment, operations and procedures, documentation, data handling, and data validation. The individual reports should be consulted for specific information.

The findings were summarized in each report as a table of recommendations given to the individual agency. The table lists deficiencies found, recommended solutions, approximate cost to implement the solutions, and an estimate of the impact of each deficiency on the quality of the data.

Approximately 50 different specific deficiencies were observed throughout the extensive evaluation period; however, for practicality and workability many specific deficiencies have been combined and reduced to more general terms for purposes of systematic and logical reporting. Table 2 lists deficiencies generically with a brief comment pertaining to each. The deficiencies are listed according to descending frequency of occurrence. Although many sites were visited at some of the agencies, no differentiation as to agency or site is attempted in this summary. The original reports must be examined for defect particularity and specificity.

TABLE 1. SUMMARY OF AIR MONITORING AGENCIES EVALUATED

Agency	Site Visited	Location
State of Arizona	Bureau of Air Quality	Phoenix, AZ
Colorado Oil Shale Tract, C <sub>a</sub>	Headquarters	Denver, CO
	Field Site #1	Rio Blanco, CO
Colorado Oil Shale Tract, C <sub>b</sub>	Field Site 023	Rio Blanco, CO
State of Colorado	Air Quality Surveillance Section	Denver, CO
	CARIH Station	Denver, CO
	CAMP Station	Denver, CO
	Arvada Station	Arvada, CO
	Welby Station	Welby, CO
	Greeley Station	Greeley, CO
	Colorado Springs Station	Colorado Springs, CO
EPA/Colstrip	Field Site	Colstrip, MT
EPA/Las Vegas (Lockheed Electronics)	Laboratory	Las Vegas, NE
State of Montana	Air Quality Bureau	Helena, MT
	Colstrip Trailer	Colstrip, MT
	Lame Deer	Lame Deer, MT
	C Hill	Anaconda, MT
	Highway Junction	Anaconda, MT
	Saddle Mountain	E. Helena, MT
	Microwave	E. Helena, MT
	Alpine West	Butte, MT
Montana Power Company	Field Site #3	Colstrip, MT
State of New Mexico	Air Quality Bureau	Santa Fe, NM
	Albuquerque Field Sites	Albuquerque, NM
	Four Corners Area Sites	Farmington, NM
NOAA/Boulder	Headquarters	Boulder, CO
(continued)		

TABLE 1 (continued)

Agency	Site Visited	Location
State of North Dakota	State Dept. of Health	Bismarck, ND
	Stanton	Stanton, ND
	Beulah	Beulah, ND
Northern Testing Laboratory	Laboratory	Billings, MT
State of South Dakota	State Laboratory	Pierre, SD
Utah Oil Shale Tracts, $U_a/U_b$	Field Site A-6	Bonanza, UT
State of Utah	Bureau of Air Quality	Salt Lake City, UT
	Price	Price, UT
	Huntington	Huntington, UT
	Salt Lake City	Salt Lake City, UT
	Magna	Magna, UT
	Bountiful	Bountiful, UT
	Ogden	Ogden, UT
	Provo	Provo, UT
Ute Research Laboratory	Laboratory	Fort Duchesne, UT
State of Wyoming	Laboratory Headquarters	Cheyenne, WY
	Newcastle Field Site	Newcastle, WY
	Gillette Field Site	Gillette, WY
	Patrick Draw Field Site	Rock Springs, WY
Yellowstone County	Laboratory	Billings, MT
	Billings Field Site	Billings, MT
	Laurel Field Site	Laurel, MT

TABLE 2. EXAMPLES OF COMMON DEFICIENCIES IN THE AIR MONITORING PROGRAMS EVALUATED

Deficiency*	Comment
1. No daily permanent record of flows, instrument parameters, instructions, remedial steps and action criteria kept by the agency.	Virtually all laboratories were remiss in some aspect of record and log book keeping. Some defects were minor but others were of major proportions.
2. Gas cylinders, permeation tubes, and other standards not NBS traceable and not rechecked upon receipt or on a scheduled basis.	Again essentially all agencies were amiss in some form or another with regards to standards traceability.
3. Poor or poorly defined intra-laboratory quality control procedures in the various tests and procedures employed.	Only a few agencies had acceptable internal quality assurance procedures.
4. Balances calibrated infrequently or not at all.	A majority of the agencies were within this category.
5. Bubbler samples handled incorrectly; flows incorrect, no leak checks made on samplers or apparatus.	Essentially all agencies that used bubblers had at least one suspect handling technique among those listed.
6. Flow rate measurement errors; instrument sample flows not monitored, altitude corrections not made.	A majority of the agencies had problems connected with the measurement and calibration of gas flows.
7. Permeation tube oven temperatures and other temperatures not measured.	Approximately half of the agencies had problems in this area.
8. Deficient calibration techniques, no zero and span charts, too infrequent zero and span of instruments, improper utilization of zero and span data.	Half of the agencies would be included.
9. Filters not conditioned properly, humidity not monitored in weighing room.	Half of the agencies had improper technique in regards to these areas.

(continued)

TABLE 2 (continued)

Deficiency*	Comment
10. NO-NO <sub>x</sub> Converter efficiency not checked.	A deficiency was exhibited by half of the agencies.
11. Zero air not analyzed for purity.	Fifty percent of the agencies did not check their air.
12. Substandard equipment or laboratory facilities.	Seven instances of such problem areas were observed.
13. Ozone generators not checked for stability.	Five agencies did no stability monitoring.
14. Recorders not calibrated or linearity checked.	Five instances of this defect were noted.
15. Safety violations of a serious enough nature to mention.	Five agencies had one or more apparent violations of good safety practice.
16. High Volume sampling method incorrect or flows or orifices not Roots-meter-calibrated.	Five agencies had incorrect practices in this category.
17. Too infrequent multipoint calibrations, or calibrations not done at the correct levels.	Deficiency noted in four agencies.
18. Poor permeation tube techniques; no air flow while being stored.	Three agencies were found to have errors in this area.
19. No spare instruments for inter-changing.	Most agencies have no spares.
20. NO <sub>2</sub> channel not calibrated correctly, KI titration errors; metal analysis errors; manifolds dirty or incorrectly constructed, poor operator training, filters handled improperly.	Several agencies had these or similar defects noted in their operations.

\* For more detailed information on site instrumentation and/or methods, the reader is directed to Site Evaluation reports available from EPA files.

Many of the deficiencies noted are of a fundamental and critical nature; other deficiencies are judgmental in nature and may or may not have impact on the data. For example, a very common deficiency listed near the top of the table is that gas cylinders, permeation tubes, and other standards are not NBS traceable and are not checked independently by the agency. A non-traceable standard cylinder is not necessarily or automatically bad, but the use of such standards certainly decreases credibility and confidence in the data and raises serious questions about data accuracy. Some of the deficiencies, such as a lack of spare analyzers, affect data in the sense that spare instruments minimize down time and increase the quantity of data taken. It is recognized that the implementation of all of the recommendations, while desirable, may be neither feasible nor practical because of budgetary or other limitations. We are aware that some corrective procedures have been undertaken, but a complete substantiation of the actions taken must await future reevaluation visits. Such visits may be authorized at some future date at the discretion of the Project Officer.

It must be emphasized that not all agencies and sites share in the deficiencies mentioned in Table 2 to an equal extent. It should also be noted that no agency had zero deficiencies. Therefore, strict numerical comparisons of defects should be made with caution and by reference to the original reports. The table does provide an accurate indication of the relative frequency of types of deficiencies that are common to many of the agencies evaluated.

SECTION 3  
INTERLABORATORY PERFORMANCE SURVEYS

Regularly scheduled quality assurance laboratory performance surveys have been carried out for the following analyses or measurements:

- 1) Sulfate/Nitrate Analysis
- 2) SO<sub>2</sub> Analysis
- 3) NO<sub>2</sub> Analysis
- 4) CO Analysis
- 5) Weighing Performance
- 6) High Volume Flow Rate Measurement

In addition to the laboratory surveys, a split sample program has been carried out with one laboratory in which a large number of filters were analyzed by the laboratory and Rockwell for trace metals and the results compared.

Table 3 lists all the surveys performed in the first year of the program by date. Participating laboratories in each survey are indicated by a check (✓) mark.

For the chemical analysis survey (1-4 in the above list) Rockwell obtains from commercial vendors, either directly or through EPA, multiple sets of the appropriate samples which are then submitted for analysis to participating laboratories. Ten replicate samples are first analyzed at Rockwell, and the mean value of the analyses is by definition the "true" value with which the results of all the participants are compared.

To assure the correctness of the Rockwell "true" value, several internal and external quality control procedures are being used. Internal quality control procedures in the Rockwell laboratory include comparison of analyses of replicate samples, comparison of every new stock standard solution with the old one, duplicate calibration curves before and after analysis, analysis of quality control standards every 10 samples, and maintenance of routine quality control charts on calibration parameters to establish laboratory control limits.



TABLE 3. LIST OF INTERLABORATORY PERFORMANCE SURVEYS AND PARTICIPANTS (\*)

Agency	Survey and Date by Quarter														
	SO <sub>4</sub> <sup>=</sup> /NO <sub>3</sub> <sup>-</sup>				SO <sub>2</sub>			NO <sub>2</sub>			CO			Weighing	Hi-Vol
	4/76	1/77	2/77	3/77	4/76	2/77	3/77	1/77	2/77	3/77	4/76	1/77	3/77	1/77	1/77
Albuquerque											✓	✓	✓	✓	✓
Arizona State	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓
C-a														✓	✓
C-b														✓	✓
Colorado State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Lawrence Radiation Lab															✓
Lockheed						✓									
Montana State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓
Montana Power Co.															✓
New Mexico State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
North Dakota State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓				✓	✓
Northern Testing Lab	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓				✓	
South Dakota State					✓	✓	✓	✓	✓	✓				✓	✓
Ua/Ub														✓	✓
Ute Research			✓	✓										✓	✓
Utah State											✓	✓	✓	✓	✓
Wyoming State					✓	✓	✓	✓	✓	✓				✓	✓
Yellowstone County					✓	✓	✓				✓			✓	✓

(\*) A check (✓) means that the agency participated in the survey.

External quality control is provided by comparing the Rockwell "true" value with the mean value obtained through replicate sample analysis either by the QAB EMSL-RTP laboratory or by the vendor. This comparison is included in each report.

The evaluation of laboratory performance is done in several ways. The most direct way is to compare the concentration determined by each laboratory with the "true" value as determined by Rockwell. Linear graphs are prepared in which the laboratory values are plotted against the "true" values. The slope, intercept, and correlation coefficient for each laboratory line are then tabulated as indices of performance. Perfect agreement between a laboratory and Rockwell for all analyses results in a straight line with unit slope, zero intercept, and a correlation coefficient equal to 1.0000.

The slope of the line is a good measure of overall analytical accuracy, provided that the intercept is small compared to the concentrations being analyzed. For example, if the intercept is small, a slope of 1.05 implies a level of agreement with Rockwell of 5%.

If the slope is near 1.0, a large intercept indicates a bias in the analyses which might be caused by such errors as incorrect blank corrections or contaminations in the water supply. The magnitude of the intercept must be evaluated by comparison with the sample size. For example, if the sample size is  $10 \mu\text{g}/\text{m}^3$ , an intercept of  $1 \mu\text{g}/\text{m}^3$  represents a 10% bias.

The correlation coefficient is a measure of laboratory precision. In almost all cases the correlation coefficient is between 0.990 and 1.000, which indicates good linear correlation between the laboratory and the Rockwell analysis. Data that show a substantial amount of scatter lead to coefficients below 0.990.

A second method used to evaluate laboratory performance is to determine whether each laboratory analysis result falls within arbitrarily defined concentration ranges denoted as "sample range" and "target range". The "sample range" is intended to describe the variability in the analysis of presumably

identical samples within one laboratory but at various times and under various conditions; i.e., "normal laboratory operation". The "target range" is intended to bracket an acceptable range of variability among different laboratories and is larger than the "sample range".

Definitions of "sample range" and "target range" have not remained the same throughout the program. For most of the surveys the "sample range" and the "target range" were defined as  $\bar{R} \pm 3 \sigma$  and  $\bar{R} \pm 5 \sigma$ , respectively, where  $\bar{R}$  is the "true" value (i.e., the mean value of Rockwell's analyses) and  $\sigma$  is the standard deviation of Rockwell's replicate analyses. For CO the standard deviation  $\sigma$  is extremely small so that a more practical definition is required. For CO the "sample range" and "target range" were defined at various times as  $\bar{R} \pm r$  where  $r$  was either a constant ppm value (e.g.,  $r = \pm 0.5$  ppm), or a constant percent of  $\bar{R}$  (e.g.,  $r = \pm 4\%$ ). Of course, the value of  $r$  was not the same for the sample range and for the target range. In some of the earlier surveys for species other than CO, the same arbitrary definition of range  $\bar{R} \pm r$  was used, except that the magnitude of  $r$  changed from one survey to the next.

Because the definitions of range depend on the performance of the Rockwell laboratory through the experimentally determined value of  $\sigma$ , great care should be exercised in evaluating performance by means of the range criteria, particularly when comparing results from different surveys. The "sample range" and "target range" criteria are most useful for comparing the performance of different laboratories within the same survey.

Initially, brackets of  $\pm 3 \sigma$  and  $\pm 5 \sigma$  were arbitrarily defined. However, since much data are now available, Rockwell is currently tabulating and analyzing this data with the view to establishing new target range criteria based on a statistical review of past performance by all the participating laboratories, including Rockwell.

Each type of survey will be discussed separately below.

#### Sulfate/Nitrate Analysis

The sulfate/nitrate performance survey requires participating laboratories to analyze a set of four to six filter strips spiked with varying amounts of sulfate and nitrate ions. At least 10 sets of filters presumed to be identical

to those analyzed by the laboratories are analyzed by the Rockwell Chemistry Laboratory using the methylthymol blue procedure for  $\text{SO}_4^{=}$  and the copperized cadmium reduction method for  $\text{NO}_3^-$ . In the interpretation of results no bias or adjustment is made for the fact that laboratories included in the surveys use methods different from Rockwell. All laboratories use EPA approved methods which give presumably equivalent results, making such adjustments unnecessary.

Tables 4 and 5, taken from the 2nd quarter 1977 report, list the linear parameters observed in the first three surveys of the contract year. To preserve anonymity, the identities of the laboratories are not shown. (There is no correlation between the identity codes in the various tables of this report. Thus Agency A in one table is not necessarily the same as Agency A in another table.) Tables 4 and 5 show that approximately one-third of the slopes are in the range of 0.95 to 1.05 (indicating deviations of 5% or less), and approximately one-third to one-half of the slopes are less than 0.90 or greater than 1.10. Analytical problems are clearly indicated if the slope falls outside the latter range.

According to Tables 4 and 5, approximately 70% of the analyses show intercepts of less than  $1 \mu\text{g}/\text{m}^3$  for  $\text{SO}_4^{=}$  and less than  $0.33 \mu\text{g}/\text{m}^3$  for  $\text{NO}_3^-$ . These intercepts should be evaluated with respect to the sample sizes, which were  $30 \mu\text{g}/\text{m}^3$  or less for  $\text{SO}_4^{=}$  and  $10 \mu\text{g}/\text{m}^3$  or less for  $\text{NO}_3^-$ . A potential analytical problem is indicated if the intercepts are significantly greater than the values mentioned above.

The correlation coefficient was less than 0.990 for three  $\text{SO}_4^{=}$  entries and three  $\text{NO}_3^-$  entries. Three of the six linearity problems involve one laboratory, and two involve another laboratory.

### SO<sub>2</sub> Analysis

SO<sub>2</sub> samples consist of standard ampules containing freeze-dried solutions of sodium sulfite and tetrachloromercurate. The "true" value for each sample was obtained by the Rockwell laboratory by analysis of at least 10 replicate samples. The usual quality control procedures were used for each analysis.

TABLE 4. SUMMARY OF RESULTS OF SO<sub>4</sub><sup>=</sup> SURVEYS

Agency Code	Quarter/Year	Slope	Intercept	Correlation Coefficient
A	4/76	-	-	-
	1/77	-	-	-
	2/77	1.0054	0.3327	0.9994
B	4/76	0.8097	1.0663	0.9963
	1/77	1.3508	-2.9730	0.9939
	2/77	1.1020	-1.2856	0.9922
C	4/76	1.0538	-0.0123	0.9964
	1/77	1.0871	0.1471	0.9930
	2/77	0.8692	0.5557	0.9972
D	4/76	0.8282	1.5705	0.9980
	1/77	1.0300	0.0747	0.9843
	2/77	1.0458	0.4330	0.9984
E	4/76	1.0355	-0.1941	0.9995
	1/77	0.8952	0.7181	0.9985
	2/77	0.9127	-0.5646	0.9989
F	4/76	0.6431	4.1915	0.9549
	1/77	1.0747	0.8746	0.9876
	2/77	1.8603	2.2721	0.9923
G	4/76	0.9260	0.0751	0.9951
	1/77	1.0313	0.4593	0.9946
	2/77	0.7555	0.9818	0.9942
EPA/QAB	4/76	1.0327	-0.1157	0.9999
	1/77	1.0528	-0.1898	0.9998
	2/77	0.9457	0.2899	0.9972

TABLE 5. SUMMARY OF RESULTS FOR NO<sub>3</sub><sup>-</sup> SURVEYS

Agency Code	Quarter/Year	Slope	Intercept	Correlation Coefficient
A	4/76	-	-	-
	1/77	-	-	-
	2/77	1.3440	-0.0604	1.000
B	4/76	1.0267	0.3102	0.9981
	1/77	1.0118	0.9563	0.9991
	2/77	0.8835	0.3492	0.9996
C	4/76	1.0511	-0.0590	0.9998
	1/77	1.0250	-0.3482	0.9770
	2/77	0.7795	.2920	.9589
D	4/76	0.9411	0.5791	0.9957
	1/77	0.8447	0.2034	0.9968
	2/77	0.8778	-0.0697	0.9990
E	4/76	1.2492	-0.2033	0.9952
	1/77	0.8781	0.0175	0.9977
	2/77	0.9136	-0.0054	0.9905
F	4/76	-2.1799	44.6805	-0.2331
	1/77	1.0497	1.0345	0.9994
	2/77	2.0848	0.0130	0.9998
EPA /QAB	4/76	1.0178	-0.0032	1.0000
	1/77	1.0504	0.1670	0.9999
	2/77	0.9479	-0.0378	0.9994

Table 6, taken from the 3rd quarter 1977 report, summarizes the SO<sub>2</sub> results for the first three SO<sub>2</sub> surveys. In all but two entries the slope was between 0.85 and 1.11, and the correlation coefficient was between 0.990 and 1.000.

The SO<sub>2</sub> sample concentration ranged from 16 to 227 µg/m<sup>3</sup>. Intercepts of greater than 10 µg/m<sup>3</sup> are of concern, and they were found in about 23% of the analyses.

### NO<sub>2</sub> Analysis

NO<sub>2</sub> samples consist of standard ampules containing solutions of sodium nitrite. The "true" value for each sample was obtained by the Rockwell laboratory by analysis of at least 10 replicate samples. The usual quality control procedures were used for each analysis.

Table 7, taken from the 3rd quarter 1977 report, summarizes the NO<sub>2</sub> results for the first three NO<sub>2</sub> surveys. In all but four entries the slope was between 0.87 and 1.09. Samples in all surveys were 0.9 µg/ml or less; therefore, intercepts greater than  $\pm 0.04$  µg/ml are of concern. Approximately 25% of the entries show intercepts in excess of these limits. The correlation coefficient was below 0.990 in only three entries.

### CO Analysis

CO samples are contained in 0.85 m<sup>3</sup> (30 ft<sup>3</sup>) aluminum cylinders. Three different concentrations were submitted for analysis in each survey. Replicate analyses were performed in the Rockwell Quality Assurance laboratory using a Bendix nondispersive infrared analyzer, and an NBS SRM cylinder containing 95.0 ppm CO in air was used as the standard. The "true" value was established by analysis of at least five cylinders of each concentration.

The results of the first three surveys were for the most part very satisfactory. Table 8 shows slopes and intercepts for each survey. Multiple entries under each agency signify that the unknown cylinders were analyzed at more than one site. As shown in the table the majority of the indicated slopes are in the range 0.95 to 1.05, and the intercepts are usually less than 1 ppm.

TABLE 6. SUMMARY OF RESULTS OF SO<sub>2</sub> SURVEYS

Agency	Survey Quarter	Slope	Intercept	Correlation Coefficient
A	4th '76	1.3483	-10.9745	0.9605
	2nd '77	1.0973	-8.2229	0.9990
	3rd '77	1.0178	-10.4733	0.9935
B	4th '76	0.9627	1.6888	0.9990
	2nd '77	0.9769	0.2874	0.9997
	3rd '77	0.9226	-0.6433	0.9987
C	4th '76	1.0618	-5.9543	0.9963
	2nd '77	0.9311	3.0098	0.9994
	3rd '77	0.9947	-12.0752	0.9999
D	4th '76	0.8757	-0.1165	0.9993
	2nd '77	0.6677	7.4901	0.9590
	3rd '77	0.8883	4.7308	0.9986
E	4th '76	0.9804	2.4875	0.9995
	2nd '77	0.9708	-2.0890	0.9992
	3rd '77	0.9373	1.2077	0.9989
F	4th '76	1.1123	-0.4824	0.9978
	2nd '77	1.0052	-1.4080	0.9997
	3rd '77	1.0316	0.7284	0.9986
G	4th '76	0.9489	-8.9719	0.9999
	2nd '77	1.0130	-14.0940	0.9989
	3rd '77	0.9103	-5.9870	0.9967
H	4th '76	1.0995	-15.6153	0.9975
	2nd '77	—	—	—
	3rd '77	0.8618	10.9976	0.9911
I	4th '76	1.0114	0.5971	0.9997
	2nd '77	1.0000	-2.4845	0.9990
	3rd '77	0.9781	-4.8377	0.9999
EPA/QAB	4th '76	0.9741	2.854	0.9994
	2nd '77	0.9447	3.3206	0.9996
	3rd '77	0.9798	-3.3785	0.9998



TABLE 7. SUMMARY OF RESULTS OF NO<sub>2</sub> SURVEYS

Agency	Quarter/ Year	Slope	Mean Slope and Rel. Std.Dev.	Intercept	Correlation Coefficient
			All Surveys		
A	1/77	1.0276	1.0214	-0.0329	0.9978
	2/77	1.0000	1.9%	-0.0282	0.9998
	3/77	1.0367		-0.0516	0.9937
B	1/77	0.9457	0.9484	0.0230	0.9992
	2/77	0.9669	1.8%	-0.0290	0.9973
	3/77	0.9326		0.0141	0.9996
C	1/77	1.2608	1.0267	-0.0336	0.9818
	2/77	0.8787	20.0%	-0.0201	.9996
	3/77	0.9406		-0.0207	0.9904
D	1/77	1.0085	0.9385	-0.0041	0.9999
	2/77	0.9872	11.0%	-0.0179	0.9979
	3/77	0.8198		0.0475	0.9990
E	1/77	1.0862	1.0042	0.1362	0.9699
	2/77	0.9955	7.8%	0.0250	0.9999
	3/77	0.9309		0.0169	0.9997
F	1/77	0.9176	0.8968	0.0070	1.0000
	2/77	0.9319	5.5%	0.0135	0.9990
	3/77	0.8409		0.0498	0.9970
G	1/77	0.9606	0.9669	0.0308	0.9993
	2/77	0.9757	0.8%	-0.0285	0.9975
	3/77	0.9645		0.0190	0.9988
H	1/77	0.9807	0.8844	0.0178	0.9997
	2/77	0.7632	12.5%	0.0515	0.9260
	3/77	0.9093		0.0506	0.9990
EPA/QAB	1/77	0.9319	0.9273	0.0101	0.9992
	2/77	0.9237	0.5%	-0.0071	0.9979
	3/77	0.9263		0.0081	0.9995

TABLE 8. SUMMARY OF RESULTS FOR CO SURVEYS

Quarter/Year	4/76		1/77		3/77	
Agency	Slope	Intercept	Slope	Intercept	Slope	Intercept
A	1.0257	0.9354	1.0342	0.4461	1.0607	0.1377
	1.0257	0.9354	1.0471	0.1439	1.0068	-1.1833
	1.0324	-0.1100			1.0272	1.0887
	1.0324	-0.1100				
	1.0257	0.9354				
	1.0394	0.4687				
B	1.0652	-0.2943	1.0633	0.0302	1.0875	0.0086
	1.2002	-1.1073	1.0445	0.2044	1.0332	-0.0318
	1.0567	0.0575	1.0474	-0.1975	1.0310	0.0005
	1.0453	0.1744	1.0467	-0.0146	0.9665	0.4786
	0.9976	-0.1519	1.0578	-0.1075		
C	1.0433	-0.8187	1.0603	0.0004	1.1229	-0.3214
	0.9948	-0.4227	1.0847	-0.4361	1.1290	-0.8475
			1.0921	-1.0442		
D	1.0389	-0.3520	0.9676	0.0054	1.0757	-2.213
	0.9839	0.5149	0.9676	0.0054		
	0.9696	0.1609				
E	0.9885	-0.1849	0.9934	0.4011	1.0945	-1.405
	0.9860	0.6367	1.0020	-0.1996	1.0073	0.5545
	0.9976	-0.9519	0.9462	-0.0036	1.0672	-1.466
	0.9745	0.6536	0.9571	-0.1308	0.9855	0.2675
	0.9977	-0.2198	0.9805	0.2032	1.0017	-1.0465
	0.9855	-0.0198	0.9656	0.0026	1.0155	0.7633
	1.0024	0.1767	1.0026	-0.3653	0.9858	0.2261
	1.0234	-1.1968	0.9941	0.7182		
			0.9669	0.6882		
F	0.9562	0.9692				
G			0.8871	0.7766	0.9799	0.2982
			0.9908	-0.1385	0.9909	-0.1266

The good agreement between the various agencies and Rockwell is probably due to the fact that agencies use cylinders for calibration that contain CO at ambient levels and require no dilution. The CO concentrations supplied by vendors are apparently sufficiently reliable for this particular analysis.

#### Weighing Survey

For this survey 12 sets of 3 "weights" each were purchased, each containing a 1, 2, and 5 g mass. All weights were modified slightly by filing away some of the mass. After thorough cleaning, each weight was weighed several times on two different balances (one capable of weighing to 0.01 mg and the other a microbalance) over a period of several days. Each balance was calibrated just prior to use with an NBS certified set of Class S weights. One set was sent to each participating agency, which then weighed the objects and reported results to Rockwell. The objects were reweighed after return to insure that no significant change had occurred during transit.

The results of the weighing survey are summarized in Table 9, which is taken from the first weighing survey report. Table 9 shows differences between the weight reported by the agency and the weight determined by Rockwell. Except for three agencies, all measurements agree with Rockwell to within 1 mg or better. The average deviation, excluding the three agencies showing large discrepancies, is less than 0.3 mg.

At least one of the three agencies with large deviations has determined that the problem was faulty balance operation and has taken steps to correct the problem. It is not known what the other two agencies have done in regard to this problem. A second weighing survey is scheduled to begin late in 1977. Other weighing surveys will be repeated semi annually if they are deemed necessary.

#### High Volume Flow Rate Measurement

One of the required tasks in the program is to conduct semi annual audits of the flow rate calibration of high volume samplers as performed by the participating agencies. For this purpose Rockwell submitted audit devices to participating agencies together with a test protocol. Agencies used the devices and at the same time performed a normal calibration. Agencies reported their measured flow rates as well as additional pressure and temperature data from

TABLE 9. SUMMARY OF WEIGHING SURVEY

Agency	Deviations from Rockwell in mg		
	1g	2g	5g
A	-0.3	0.0	0.4
B	-0.2	-0.2	-0.2
C	0.2	0.1	-0.1
D	-0.4	0.5	-0.5
E	-0.5	-0.6	-0.1
F	0.2	0.1	0.2
G	0.9	0.3	0.2
H	1.9	1.9	1.9
H (reweigh)	0.0	2.0	1.8
I (balance A)	-0.1	-0.1	0.0
I (balance B)	-0.1	0.0	0.2
J	2.6	2.8	1.9
K	-0.3	-0.3	-0.2
L	-0.1	-1.0	-0.8
M	-0.2	0.0	-0.3
N	-1.8	-1.9	-2.2
N (reweigh)	-1.7	-1.6	0.0
O	0.1	-0.1	-0.1
QAB EMSL/RTP	-0.4	-0.3	-0.2

which Rockwell calculated "true" flow rates. The results of the comparison between values measured by each agency and calculated by Rockwell are summarized in Table 10. This table gives each agency's calibration error, which is defined as the percent difference between the indicated flow and the "true" flow, measured at  $1.132 \text{ m}^3/\text{min}$  ( $40 \text{ ft}^3/\text{min}$ ).

Significant discrepancies were found in several of the sites, and specific recommendations were proposed in the report to study the causes for the discrepancies. A basic problem appears to be a lack of definite, uniform set of instructions, approved by EPA, which is specific for the various types of calibration and measuring equipment used by the agencies. One evidence of this is that some agencies report flows converted to standard conditions while others report flow at ambient conditions. In many cases the basis for the flow measurement is ambiguous, especially if no temperature or pressure corrections are made. Further evidence of a lack of uniform instructions is the large number of errors that were discovered after the preliminary survey results were sent to the agencies. Although it is possible that some of the errors were caused by instructions from Rockwell which were not absolutely clear, it is also apparent that operators are not all thoroughly familiar with calibration procedures and the means for converting scale reading to actual flow.

A specific problem in the high-volume audit occurred in two sites which use flow controllers. In these sites the flow appeared to change drastically when the different resistance plates were attached to the audit fixture. Since the report was written, it was determined that this anomaly was an artifact generated by the audit fixture, and an investigation is currently under way to eliminate this problem in the next survey, which is scheduled for late in 1977.

#### Analysis of Metal Samples From Laboratory A

One of the requirements of the Western Quality Assurance Program is to duplicate approximately 10% of the analyses performed by a designated laboratory (denoted here as Laboratory A) for metals collected with particulates in high-volume samplers. The method of analysis is atomic absorption, and the elements that were originally listed included Be, Ca, B, Zn, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, and Ni.

TABLE 10. SUMMARY OF RESULTS IN THE HIGH VOLUME SURVEY

Agency	No. Reporting Sites	Error %		Remarks
		Min.	Max.	
A	13	-21.2	9.2	Scatter between sites is of concern and should be investigated further.
B	1	-4.6		Agency's calibration is satisfactory.
C	1	-2.2		Agency's calibration is good.
D	1	-1.0		Agency's calibration is excellent.
E	1	-11.4		Calibration is fair.
F	1	XXXX		Agency uses flow controller. Flow appeared to change drastically when resistance plates were changed. Anomalous effect subsequently traced to unsuitable audit procedure.
G	3	6.5	25.0	Several errors in the measurement had to be corrected. High intercept should be investigated further.
H	1	0.4		Agreement is excellent.
I	1	-0.9		Agreement at $1.132 \text{ m}^3/\text{min}$ is excellent. However, slope and intercept are far from ideal. May have a calibration problem.
J	1	-1.7		Agency's calibration is excellent.
K-1 to K-5	5	-12.8	-8.8	Agency's calibration data are internally consistent among the sites, but all are low by about 10% compared to Rockwell.
K-6 to K-10	5	6.7	26.8	Agency's calibration data are internally consistent among the sites, but all are high compared to Rockwell. An error in reading of manometer is suspected. Agency concurs with this assessment.

(continued)

TABLE 10. (continued)

Agency	No. Reporting Sites	Error %		Remarks
		Min.	Max.	
L	1	-1.4		Agency's calibration is excellent.
M	2	-8.4	-7.9	Agency's calibration is satisfactory. There is an apparent small constant negative bias in the calibration data.
N	3	25.9	38.8	All agency's calibrations show a large, positive bias. Problem is serious and requires investigation.
O	1	-0.1		Agreement is excellent.
P	2	XXX		Agency uses flow controller. Flow appeared to change drastically when resistance plates were changed. Anomalous effect subsequently traced to unsuitable audit procedure.

At least 3 sets of samples were received from Laboratory A during the first year of the contract. The first set was analyzed in December 1976, but some difficulty was encountered in comparing results with those of Laboratory A because of uncertainty concerning the history of the filters. Of all the metals listed above, Rockwell could obtain valid data only for Cu, Fe, and Mn, since the rest of the trace elements were below the detection limit. For the three elements that were measured, plots of Laboratory A data vs Rockwell data showed very large scatter.

Analysis of a second and third batch of filter samples disclosed the following problems:

1. High and variable blanks for Cu, Fe, Mn, and Ni, suggesting contamination in handling.
2. Concentration levels for Cd, Co, Cr, Mo, and Ni were either below the Rockwell detection limit or at such low values that analysis could not be performed with better than  $\pm 50\%$  accuracy; thus no comparisons could be made. In many cases the values reported by Laboratory A were also very low.
3. Comparison plots for Cu, Fe, Pb, and Mn show a large amount of scatter.

The cause for the discrepancies between the Laboratory A and the Rockwell analyses is not known. In order to investigate the origin(s) of the differences, a test program was designed, and, with the concurrence of the Project Officer and Laboratory A, was initiated during September 1977. The test consists of a sample exchange program in which synthetic metal samples prepared by Rockwell will be analyzed by both Laboratory A and the Rockwell Chemistry Laboratory. Three types of samples were chosen in order to investigate three general sources of discrepancies: contamination, extraction, and analytical procedures. The samples included are as follows:



1. Uncut blank filters.
2. Spiked filters containing known concentrations of Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, and Pb. The concentrations are chosen to be significantly above detection limits.
3. Solutions of the above metals dissolved in 10% HNO<sub>3</sub>.

In addition to the above analyses, all of the liquid extracts analyzed by Laboratory A will be returned to Rockwell for reanalysis.

Extensive reporting forms have been designed to obtain a large amount of information from Laboratory A concerning its analytical and quality control procedures. From an evaluation of the Laboratory A procedures and the results of the analyses of all the samples, it should be possible to isolate and perhaps identify problems that are traceable to contamination, extraction, or analytical procedures. Results from this task will be made available in the next report together with all pertinent forms and procedures.

## SECTION 4

### FIELD AUDITS

As an integral part of the Western Quality Assurance Program, regularly scheduled audit trips are conducted by Rockwell personnel to various sites throughout the country; most of the sites are in the western states where various energy sources are being developed. Table 11 shows a list of all the sites audited and the dates of the audits.

The audit procedure consists of delivering to each analyzer five different concentrations of analyte, including zero, using a portable audit device. The output of the analyzer is measured with a digital voltmeter or with the measuring device used in the station. The result of each audit is a five-point response curve which is graphed and compared with the latest calibration curve in use at the station. To distinguish between the audit curve and the station calibration curve, we sometimes refer to the audit results as the "calibration audit". It should be understood that the constants derived from the audit curve are used by Rockwell, EPA, and the agency for evaluating the station calibration. The "calibration audit" is not intended to give a substitute calibration for use by the agency for data reduction. Differences between the station calibration and audit results are given either as a percent calculated at full scale, or as differences in calibration and audit constants. Where the differences are unusually large, an attempt is made to locate the source of the problem.

The audit devices used in the audits are portable calibrators designed and built at the Rockwell Air Monitoring Center. These audit devices are capable of generating and delivering mixtures of various gaseous pollutants in air at precisely known concentrations. Since flows are reproducible and accurate to  $\pm 1\%$ , dilution of pollutants is known to  $\pm 2\%$  over a 3000 to 30 dilution range. Mixtures are produced either by dilution of gases contained by cylinders, by means of an ozone generator, by gas phase titration, or by dilution of gases diffusing from permeation devices. Standards are traceable either directly or secondarily to the National Bureau of Standards (NBS). (For further detailed information the reader is directed to the Standard Appendix attached to any Audit Report.)

TABLE 11. SUMMARY OF AUDITS PERFORMED BY ROCKWELL DURING THE PERIOD  
AUGUST 1976 TO SEPTEMBER 1977.

Agency	Site	Date
C-a	1	Dec. 1976; April 1977; Aug. 1977
C-b	023	Dec. 1976; April 1977; Aug. 1977
State of Colorado	CARIH	Dec. 1976; April 1977; July 1977*
	CAMP	July 1977*
	Greeley	July 1977*
	Arvada	July 1977*
	Colo. Springs	July 1977*
EPA/EMSL	RTP	May 1977; Aug. 1977
EPA/Corvallis	Colstrip	Sept. 1977
L.L.L.	Imperial Valley	March 1977; May 1977
State of Montana	Colstrip	Sept. 1976; June 1977; Sept. 1977
	Billings	Sept. 1976; March 1977; June 1977; Sept. 1977
	Laurel	Sept. 1976; March 1977; June 1977; Sept. 1977
	C Hill	June 1977; Sept. 1977
	Highway Junction	June 1977; Sept. 1977
	Microwave	June 1977; Sept. 1977
	Saddle Mountain	June 1977
	Butte	Sept. 1977
State of New Mexico	Farmington	Feb. 1977
	Water Tank	Feb. 1977
	Shiprock	Feb. 1977
	Reservation	Feb. 1977
NOAA	Boulder	Dec. 1976; April 1977; July 1977
State of North Dakota	Stanton	Dec. 1976; April 1977; Sept. 1977
	Bismarck	Sept. 1977
Ua/Ub	A6	Nov. 1976; April 1977; Aug. 1977
State of Utah	Price	Nov. 1976; April 1977, Sept. 1977
	Huntington	Nov. 1976; April 1977, June 1977 Sept. 1977
	Salt Lake City	June 1977; Sept. 1977
	Magna	June 1977; Sept. 1977
	Bountiful	June 1977
	Ogden	June 1977, Sept. 1977
	Provo	June 1977; Sept. 1977
State of Wyoming	Patrick Draw	Nov. 1976; April 1977; Aug. 1977

\* No audit report was issued for this audit because of technical problems.

The portable audit devices are checked in the laboratory prior to and at the conclusion of each audit trip. Tests include a multipoint flow calibration check for the flow controller and a full performance test in which the portable audit device is compared with a fixed laboratory calibrator. The latter test is carried out as follows. The response of an analyzer in ppm/volt is determined twice by performing consecutive one point calibrations with the same calibration standards, using first the fixed calibrator and then the portable device. Performance checks are made for NO, NO<sub>2</sub>, O<sub>3</sub>, and SO<sub>2</sub>. In this way all functional components of the calibrator are checked. Ideally the ratio of analyzer response measured with the two devices should be 1.00. Since four independently calibrated flow controllers are involved, each having a maximum uncertainty of  $\pm 1\%$ , the portable calibrator is judged to be in good order if the response ratio is between 0.96 and 1.04. Usually the observed response ratio is between 0.98 and 1.02. A faulty solenoid valve, a leak in the system, contamination in the lines, an erroneous flowmeter calibration, or any other conceivable failure mode would be expected to cause the experimentally determined response ratio to deviate significantly from 1.00, and corrective action would then be necessary.

In addition to the audit of the continuous analyzers, checks are also made on the high volume flow rate and on some of the meteorological instruments. The high volume flow rate is checked using a calibrated orifice plate.

Each instrument audit results in a comparison between the station calibration curve and the audit calibration curve. Normally, response is linear. Where single point audits are made (e.g., Hi-vol sampler), the response is assumed linear. If deviations from linearity or zero differences are observed, they are specifically mentioned in the audit report.

Criteria for evaluating differences between station measurements and audit results are not rigidly defined and have never been established. The definition of "satisfactory" or "unsatisfactory" agreement is necessarily arbitrary and depends on the intended use of the data as defined by both the agencies involved and the EPA.

For the purposes of the Rockwell audits, the following working guidelines have been adopted:

Discrepancies of 10% or less at full scale require no specific corrective action and may be considered "satisfactory".

Discrepancies in excess of 10% at full scale are of immediate concern. In such cases, Rockwell will make a specific attempt to locate the source of the problem and, if this is not practical, likely sources of error will be identified and recommendations will be made to the agencies for further study. A typical recommendation of this type is to request the agency to recalibrate (or calibrate for the first time) the analyzer in question.

An additional check on the Rockwell equipment and procedures is made by means of the quarterly audits performed in the EPA/EMSL laboratory at Research Triangle Park (RTP), N.C. These special audits are designed to compare standards and procedures between Rockwell and EPA. During the first year of the program, two audits of the EPA laboratory were made. Checks were made for NO, NO<sub>2</sub>, O<sub>3</sub>, CO, CH<sub>4</sub>, and SO<sub>2</sub>. Except for one ozone audit, in which an analyzer operational problem was identified, differences at full scale were always less than 5%.

During the first year of the program approximately 70 audits were performed; hence, a very large amount of data has been collected. To evaluate the performance of each agency, the individual audit available in EPA files should be consulted. Table 12 gives a summary of overall performance by instrument type. Table 12 shows the spread of the results in the column labeled "Range of Discrepancies in %". Although the largest positive and largest negative differences are quite dramatic, another measure of the agencies' accuracy relative to Rockwell can be seen by examining the average discrepancy calculated without regard to sign. Column 4 shows the percentage of the audits that are considered satisfactory by virtue of the fact that the discrepancy was 10% or less.

Table 12 demonstrates that of all continuous analyzers agencies are most successful in calibrating CO, CH<sub>4</sub>, and THC analyzers. In the case of CO, 86% of all audits results showed full-scale differences of 10% or less. This conclusion is consistent with the results obtained in the interlaboratory performance survey for CO analysis. As indicated previously in Section 3

TABLE 12. SUMMARY OF AUDIT RESULTS \*\*

(1) Parameter measured	(2) Number of audits	(3) Range of Differences in %			(4) Percent of audits with 10% or less discrepancy
		Max	Min.	Ave *	
NO	31	78	-28	16.7	55
NO <sub>x</sub>	28	97	-34	16.5	50
NO <sub>2</sub>	23	36	-78	18.2	43
O <sub>3</sub>	35	27	-30	9.8	66
CO	21	57	-11	8.6	86
SO <sub>2</sub>	65	84	-70	14.5	57
CH <sub>4</sub>	8	8	-12	6.9	75
THC	14	103	-6	13.9	71

\* Average discrepancy without regard to sign

\*\* Further breakdown of these data by site, agency or station is given in the audit reports for various agencies. All reports are available in EPA files.

and Table 8, the majority of CO cylinder analyses were accurate to  $\pm 5\%$ . The obvious explanation for this observation is that most agencies calibrate these instruments by means of span cylinders which require no dilution and a minimum of handling. In most cases each site has its own span cylinder; hence, calibrations are done frequently.

The most unsatisfactory results are found in the audit of NO<sub>2</sub>, NO<sub>x</sub>, NO, and SO<sub>2</sub> analyzers. To calibrate these instruments, portable calibrators are normally used to prepare dilutions from concentrated mixtures or from permeation devices. Portable calibrators are generally in short supply, and their use requires personnel with some degree of skill and experience. Conclusions that could be drawn from the results in Table 12 are as follows:

- (1) Greater emphasis should be given to checking the integrity of the portable calibrator.
- (2) Calibration of these analyzers should be performed more frequently.
- (3) Greater care should be taken to insure that any given operator is familiar with calibrator operation and its correct use.

## SECTION 5

### TECHNICAL ASSISTANCE

In accordance with the provisions of the contract, Rockwell has provided technical assistance to the various participating agencies, as requested by the Project Officer. Some of the assistance has been relatively minor, consisting of instruction manuals, procedures, or literature references relating to chemical analysis and quality assurance sent to agencies on request. Much of the technical assistance in air pollution monitoring was given informally during site evaluation and field audit trips when extensive discussions and information exchange between Rockwell and agency personnel took place.

The following is a list of major interactions with various agencies during which Rockwell provided technical assistance. The identity code in this section is not necessarily the same as that in other sections (Agency A here is not necessarily the same agency as Agency A mentioned in other sections).

#### AGENCIES ASSISTED

##### Agency A

Assistance was given Agency A in modifying its trailer and monitoring procedures. (October 1976.)

##### Agency B

Personnel from Agency B visited Rockwell to discuss quality assurance procedures, AA analysis procedures, and use of the Technicon Analyzer for  $\text{SO}_4^{=}/\text{NO}_3^{-}$  analysis (November 1976 and September 1977).

##### Agency C

Information was supplied to Agency C concerning QA procedures in air monitoring programs, including calibration procedures and calibration standards. Assistance was also provided to establish a quality assurance program in the analytical chemistry laboratory (November 1976).



The site evaluation report and the first audit results were discussed with legal personnel from the Agency. Additional discussions were held with air monitoring personnel concerning quality assurance procedures (January 1977).

Written procedures for the analysis of  $\text{SO}_4^{=}$ ,  $\text{NO}_3^-$ , and arsenic were sent to the agency's laboratory upon request (April and August 1977).

Split sample filters were received from Agency C and analyzed for trace metals. The comparison with the agency's analysis disclosed good agreement for Cd, Cu, Fe, Pb, and Zn but not for Al (June and July 1977).

Information was given to the agency's chemistry laboratory to assist it in setting up a Technicon analyzer and to develop the analytical procedures for arsenic (June and July 1977).

A set of class S weights was purchased and delivered to the agency's laboratory (July 1977).

#### Agency D

A cylinder containing approximately 15900 ppm CO was analyzed by comparison with an NBS standard. The CO cylinder is being used as the agency's CO standard (April 1977).

A detailed set of instructions for performing ozone calibrations by means of the gas phase titration technique was written and sent to Agency D (May 1977).

#### Agency E

A Bendix portable calibrator belonging to Agency E was checked in the Rockwell quality control laboratory. Several major plumbing deficiencies were discovered, and specific recommendations were made to rectify the problems (May 1977).

Written instructions describing analysis of arsenic and selenium, as well as filter extraction procedures, were sent to Agency E upon request (June 1977).

#### Agency F

A detailed set of instructions for performing ozone calibrations by means of the gas phase titration technique was written and sent to Agency F (May 1977).

A study was performed in the Rockwell quality control laboratory to develop the procedures for calibrating ozone analyzers by means of the reverse gas phase titration technique. These procedures are needed because many of the stations operated by this agency do not have a NO-NO<sub>x</sub> analyzer; thus, the normal gas phase titration technique cannot be used (August 1977).

Two cylinders containing CH<sub>4</sub> in air were analyzed by comparison with an NBS standard and sent back to Agency F. The cylinders are used by the agency as hydrocarbon standards (July 1977).

A plumbing modification was designed and plans were sent to Agency F to help it improve its CO and HC sampling system. The modification is desirable to reduce waste of calibration gas and to improve audit capability (August 1977).

#### Agency G

Agency G requested information on SO<sub>2</sub> analyzers, calibration equipment, data reduction hardware, and meteorological instrumentation. The requested information was sent to the agency (July 1977).

A set of class S weights was purchased and delivered to the agency's laboratory (July 1977).

#### Agency H

Agency H requested assistance in setting up a new Technicon analyzer. Assistance was given in telephone conversations between Agency H and Rockwell laboratory personnel (August 1977).

#### Agency I

A special study was conducted in August 1977 in the Rockwell quality control laboratory with personnel from Agency I to determine the cause for the large discrepancies in SO<sub>2</sub> calibrations found in field audits of stations

operated by Agency I. A procedural error in the calibration method used by Agency I was found which largely accounted for the audit discrepancies. Agency I has subsequently modified the procedure to eliminate the error (August 1977), as evidenced by subsequent field audit results.

#### EPA/EMSL, RTP

A special joint study was conducted at EPA's request in the Rockwell quality control laboratory with Mr. Ken Rehme of the EPA/EMSL/RTP laboratory to evaluate a new procedure for calibrating ozone analyzers based on a boric acid/KI absorption solution. The boric acid/KI procedure was compared with UV photometry and gas phase titration. Good correlations were obtained among the three methods (September 1977). It is understood that further work is underway under Mr. Rehme's direction to align these results with current agency-EPA policy regarding the gas phase titration technique.

#### U.S. GEOLOGICAL SURVEY WATER QUALITY FIELD STATIONS

One activity was added-on to the contract toward the end of the first year, an on-site inspection and evaluation of seven water quality field stations of the U.S.G.S. in the states of Arizona, Colorado, Montana, New Mexico, North Dakota, Utah, and Wyoming. The visits have been completed, and reports are currently being written (September 1977).

#### GENERAL REVIEW MEETING

A meeting of representatives from the participating state and private agencies, EPA, and Rockwell was held in Denver on April 26-27, 1977, to review the Western QA program. The main speakers and topics were as follows:

- S. Bromberg, EPA/EMSL/RTP. Introduction and Purpose of Meeting
- R. Williams, EPA/Region VIII. General Remarks about the Purpose of the Program
- G. D'Alessio, EPA/Washington. Energy Overview -- National
- R. Snelling, EPA/EMSL/Las Vegas. Energy Overview -- Western States
- M. Rinaldi, State of New Mexico. Energy Overview -- Regional Office
- T. Thoem, EPA/Region VIII. Energy Overview -- Regional Office
- E. Parry, Rockwell International. Laboratory Evaluation Discussion
- G. Colovos, Rockwell International. Laboratory Audit Discussion
- M. Cher, Rockwell International. Field and Laboratory Audit Discussion

In addition to hearing the above speakers, the entire group participated in general discussions on all subjects concerning the program.

## SECTION 6

### PLANS FOR NEXT YEAR

The general plans for next year are to continue the current program of laboratory performance surveys, field audits and technical assistance. Since the ultimate purpose of the contract is to help the participating agencies in improving the quality of their data base, some modifications in the program will undoubtedly become necessary. For example, it is anticipated that technical assistance efforts may be increased in order to help correct difficulties found during performance surveys and field audits. If a history of good performance warrants the phasing out of certain tasks, this ought to be done in order to concentrate efforts on specific trouble spots.

To accomplish the desired goal of the program, constant reevaluation of the program is required by Rockwell, the Project Officer, the EPA regional offices, and the participating agencies. Changes in the program will be effected whenever it seems appropriate, given the consent and cooperation of the Project Officer and all interested parties.

# **TECHNICAL REPORT DATA**

*(Please read Instructions on the reverse before completing)*

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16. ABSTRACT  This report describes and summarizes the activities during the first year of the program named above. The activities described are part of a continuing 5-year program.  The purpose of the program is to establish a quality assurance data base for ambient air monitoring in specified geographical areas around present and proposed energy development projects, and to provide technical assistance to enable existing monitoring networks to achieve a high level of data quality. An initial on-site review of 18 laboratories and associated field sites was completed. Regularly scheduled laboratory performance surveys are being carried out for the analysis of sulfate, nitrate, SO <sub>2</sub> , NO <sub>2</sub> , and CO and for weight measurement and high volume flow rate. Approximately 10% of the analysis performed by a specified laboratory for metals collected in high volume filters are being repeated in the Rockwell laboratory. Quarterly field audits are being conducted at specified monitoring sites. Technical assistance has been provided to participating monitoring groups, as requested by the Project Officer.					
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